METHOD AND DEVICE FOR GENERATING A HYDROGEN-RICH GAS

BACKGROUND AND SUMMARY OF INVENTION

[0001] This application claims the priority of German application No. 100 41 384.6, filed August 23, 2000, the disclosure of which is expressly incorporated by reference herein.

[0002] The present invention relates to a method and a device for generating a hydrogen-rich gas. The present invention relates in particular to a method for starting a gas-generation device.

[0003] Hydrogen can be generated from suitable fuels by exothermic partial oxidation, referred to below as POX, in accordance with the following equation

$$-(CH_2)- + 1/2O_2 \text{ (air)} \Rightarrow H_2 + CO$$

and/or endothermic steam reforming in accordance with the following equation:

$$-(CH_2)- + 2H_2O \text{ (air)} \Rightarrow 3H_2 + CO_2.$$

[0004] It is also possible to use a combination of the two processes, which may lead to an autothermal operating method. Suitable fuels are, in particular, methanol and other hydrocarbon derivatives, such as higher alcohols, petroleum, diesel, LPG (liquid petroleum gas) or NG (natural gas).

[0005] U.S. Patent No. 3,982,910 discloses a hydrogen generator and a method for generating a soot-free, hydrogen-rich gas by partial oxidation. To start the generator up, air

is mixed with a spray mist of liquid hydrocarbon fuel and ignited in the generator. The heat of combustion is used to preheat air which is to be supplied to a predetermined temperature. When this temperature, which is higher than the boiling temperature of the liquid fuel, is reached, operation switches over to normal operation. In normal operation, the fuel is evaporated, mixed with the preheated air and then the hydrogen-rich gas is generated from the fuel mixture of partial oxidation in a fuel chamber of the generator. When the generator is being started, the air/fuel ratio is set in such a way that it is higher than that of normal operation with evaporated fuel.

[0006] EP 0 646 093 (U.S. Patent No. 5,143,647) discloses a method for starting up a steam reforming/partial oxidation process for converting a methane-containing starting gas into a hydrogen-rich gas using a fluidized-bed or slugging fluidized-bed catalyst, in which the tendency of the catalyst material to lump together is reduced. In this method, in a first step a fluidized bed comprising inert particles, preferably of aluminium, is heated to the reaction temperature in an oxidizing atmosphere in the presence of oxygen and in the absence of a reforming catalyst. Then, a reducing atmosphere is generated, before the reforming catalyst, preferably a nickel-containing catalyst, is introduced into the fluidized bed. The starting gas is then converted into a hydrogen-rich gas at the catalyst in the presence of oxygen.

[0007] EP 0 887 306 (U.S. Patent No. 6,241,792) discloses a method for starting a gas-generation device with downstream gas-cleaning stage, in which a hydrogen-rich gas is generated from a fuel of partial oxidation and/or steam reforming. To clean the gas, a selective CO oxidation stage, which generally comprises a platinum-containing catalyst, is used. During the starting phase, the gas-cleaning stage is

temporarily used as a catalytic burner, as a result of oxygen being admixed with the fuel and the direction of flow being reversed in such a way that medium flows first through the gas-cleaning stage and then through the gas-generation device. During starting, the device is rapidly heated to operating temperature by the gas-cleaning stage, which is operated as a burner.

[0008] EP 0 924 163 (U.S. Patent No. 6,268,075) discloses a method for starting steam reforming by a reforming reactor, an evaporator, a catalytic burner and a membrane module in order to separate out hydrogen. During a cold start, a heating operation is carried out, during which, in a first operating phase, the reforming reactor and the evaporator are heated by the burner. In a second operating phase, the reforming reactor is operated with a water/hydrocarbon ratio which is higher than that used in normal operation, and the reformate gas is fed to the catalytic burner via the membrane module. In a third operating phase of the heating, the supply of hydrogen or hydrocarbon to the catalytic burner is reduced. As the operating temperature of the membrane module rises, the proportion of hydrocarbon in the hydrocarbon/steam mixture in the evaporator is increased up to the mixing ratio used during normal operation.

[0009] EP 0 924 161 discloses a method for operating an installation having a reactor which is suitable for both steam reforming and partial oxidation, an evaporator and a membrane module. A catalytic burner is provided, in order to bring the reactor, the evaporator and the membrane module up to operating temperature. When the installation is started, the reactor, in a first operating phase, is operated as a partial oxidation reactor with an operating pressure which is lower than that used in normal operation. In a second operating phase, the reactor is switched over to reforming operation,

and the pressure is increased from the heat-up operating pressure to normal operating pressure.

[0010] WO 99/31012 discloses a method for operating an installation for steam reforming of a hydrocarbon, in which part of a reforming reactor is designed as a multifunctional reactor unit. During the cold start, the multifunctional reactor unit, in a first operating phase, is operated with fuel and oxygen-containing gas supplied simultaneously, as a catalytic burner, and in a second operating phase is operated as a partial oxidation reactor (POX reactor). During the transition from the first operating phase to the second operating phase, water is metered to the fuel/oxygen mixture and/or the quantitative flow of fuel is increased as the temperature of the multifunctional reactor unit rises and/or the quantitative flow of the oxygen-containing gas is set to a substoichiometric ratio even during the first operating phase. The substoichiometric ratio is intended to promote the generation of cleaved products, such as hydrogen, by thermal decomposition of the fuel. To establish suitable conditions for the partial oxidation of the fuel in the second operating phase, the ratio of oxygen-containing gas and fuel is reduced compared to that used in the first operating phase. The remaining part of the reactor, i.e. the area which is not provided as a multifunctional reactor unit, is used as a further reforming unit and CO shift converter stage during the second operating stage. In normal operation, the multifunctional reactor unit is at least from time to time used as a reforming unit for hydrogen generation.

[0011] By contrast, an object of the present invention is generating a hydrogen-rich gas by partial oxidation and steam reforming, thereby preventing aging of the catalyst of the steam reformer.

[0012] The method according to the present invention ensures that the oxygen content in the product gas of the POX reactor is minimized in every operating phase. Unburnt oxygen fractions would oxidize the catalyst of the steam reformer and therefore lead to increased aging of the catalyst.

[0013] In an advantageous refinement of the method, the steam reformer is heated by heating means. Therefore, the heat of combustion of the fuel can substantially be used to heat the POX reactor. As a result, the POX reactor is rapidly brought to the operating temperature for the partial oxidation, so that even after a short time hydrogen-rich gas is available via the partial oxidation.

[0014] According to a further advantageous configuration of the present invention, product gas which is generated in the POX reactor is passed through an adiabatic, catalytic after-treatment stage, in order for unburnt parts of the fuel/oxygen mixture or of the fuel/oxygen/water mixture of the product gas to be converted in the after-treatment stage, so that the oxygen content in the product gas before it is fed to the steam reformer is minimized. During the burning of fuel in the POX reactor and in particular at low temperatures, unburnt fractions of the fuel/oxygen mixture may still occur in the product stream of the POX reactor. Converting these residual fractions in the after-treatment stage prevents them from being able to cause aging of the catalyst of the reformer.

[0015] A gas-generation device according to the present invention comprises at least one POX reactor with downstream steam reformer, an adiabatic, catalytic after-treatment stage being arranged between the POX reactor and the steam reformer. During starting, hydrogen-rich gas can be generated using the POX reactor after only a short time. If the POX reactor is designed suitably, the starting materials for the steam

reforming can also be heated or evaporated in the POX reactor. Unburnt oxygen fractions of the POX product stream are converted in the catalytic after-treatment stage, so that a minimized oxygen content is ensured even at the beginning of the starting phase and at low temperature, and aging of the catalyst of the reformer is counteracted.

[0016] In an advantageous refinement, the adiabatic, catalytic after-treatment stage comprises a precious-metal-containing catalyst. Precious metals, such as platinum, are catalytically active even at low temperatures and are therefore particularly suitable.

[0017] In a further advantageous refinement, the adiabatic, catalytic after-treatment stage comprises a catalyst support with a low heat capacity. As a result, the after-treatment stage can be heated to operating temperature quickly and with little consumption of thermal energy.

[0018] In an advantageous refinement, heating means are provided for heating the steam reformer and/or the adiabatic, catalytic after-treatment stage. Consequently, heating is possible independently of the heat of combustion of the POX reactor. In particular, the after-treatment stage can be brought to operating temperature at the very beginning of the starting phase, so that the oxygen content of the product gas of the POX reactor is minimized even at the start of combustion.

[0019] Other objects, advantages and novel features of the present invention will become apparent from the following detailed description of the present invention when considered in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

[0020] The sole figure shows a diagrammatic block diagram of a gas-generation device according to the present invention.

DETAILED DESCRIPTION OF THE DRAWING

[0021] The gas-generation device according to the present invention, which is illustrated in the figure, comprises a partial oxidation reactor 1 (POX reactor), a steam reformer 2, an adiabatic, catalytic after-treatment stage 3, which is connected between POX reactor 1 and steam reformer 2, and heating means 7 for heating the steam reformer 2 and/or the after-treatment stage 3.

[0022] Conventional reactors and/or reformers which are known to the person skilled in the art can in particular be used as the POX reactor and the steam reformer. The catalysts used may, by way of example, be copper-containing and/or platinum-containing catalysts. The adiabatic, catalytical after-treatment stage 3 comprises a catalyst support with a low heat capacity and a precious-metal-containing catalyst, for example based on platinum. The after-treatment stage 3 may preferably be integrated in the collector manifold (not specifically shown) of the POX reactor 1 or in the distributor manifold of the reformer 2.

[0023] Starting materials for the generation of the hydrogen-rich gas are fuel, oxygen-containing gas, and/or water. A preferred fuel is methanol. However, it is also possible to use other hydrocarbon derivatives, such as higher alcohols, petroleum, diesel, LPG (liquid petroleum gas) or NG (natural gas). The oxygen-containing gas used is preferably air. All the starting materials can be fed to the gas-

generation device via an inlet side 4 of the POX reactor 1. In this case, a feed 5 for the liquid starting materials, such as fuel and water, and a feed 6 for metering in air are provided.

[0024] To start the gas-generation device, first of all fuel is metered into the POX reactor 1. Then, air is admixed for homogeneous and/or catalytic combustion of the fuel. This order ensures that, when the device is starting, no unburnt air passes out of the POX reactor 1 into the reformer 2. The quantity of air is set in such a way that it at most corresponds to the stoichiometric ratio of complete combustion with the corresponding quantity of fuel which is supplied. This promotes complete conversion of the air in the POX reactor 1 (i.e. oxygen levels in the POX product gas are minimized). The heat of combustion which is generated is used to bring the POX reactor 1 to operating temperature. The heat of combustion can also be used to heat further parts of the installation, such as the catalytic after-treatment stage 3 or the reformer 2 to operating temperature, at least as an auxiliary measure. In order for the gas-generation device to be started rapidly, however, separate heating means, such as burners or electrical heaters, are preferred.

[0025] In the next operating phase, when the operating temperature for partial oxidation in the POX reactor 1 is reached, the quantity of air supplied is reduced, since the partial oxidation of the fuel requires considerably less oxygen than the combustion. At the same time, water is metered in, in order to prevent overheating during the catalytic combustion and to prepare for transition to the steam reforming of the fuel. In this phase, the quantity of air and/or water is regulated in such a way that complete conversion of the fuel/oxygen/water mixture into hydrogen takes place. Consequently, in this operating phase too, oxygen

levels in the POX gas caused by unburnt air constituents are minimized.

[0026] When the operating temperature of the steam reforming in the steam reformer 2 is reached, the quantity of air supplied is reduced further or the supply of air is interrupted. Consequently, only part of the fuel which is supplied is converted in the POX reactor 1. Most of the fuel is converted into hydrogen, with corresponding metering of water, in the downstream steam reformer 2, which has a better system efficiency than the POX reactor 1. It is advantageous to maintain the POX operation, since, by metering liquid fuel into the POX reactor 1, it is possible to react more quickly to load changes than by changing the quantity of the fuel/steam mixture in the reformer 2. The use of the adiabatic, catalytic after-treatment stage 3 ensures that oxygen fractions which are still present in the product gas of the POX reactor, as may occur in particular at low temperatures on account of unburnt air constituents, are catalytically converted, and this counteracts aging of the reformer catalyst 2.

[0027] The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.